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DESCRIPTION

PARTICULATE MATTER PURIFYING CATALYST5 Technical Field

The present invention relates to a catalyst for combustion removal of soot-like particulate matter (carbonaceous fine particles) contained in exhaust gas emitted from internal combustion engines such as diesel engines.

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Background Art

Exhaust gas emitted from diesel engines contains particulate matter and constitutes one of the causes of local air pollution. Reduction of particulate matter emissions is one of the major environmental issues for which a swift solution is desired.

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In order to reduce particulate matter emissions, much research is being devoted to studying systems wherein a particulate matter filter is situated in the diesel engine exhaust path to collect particulate matter in exhaust gas, and the collected particulate matter is then ignited and combusted. However, the particulate matter collected on the particulate matter filter does not ignite unless heated to a temperature of above approximately 600°C, whereas diesel engine exhaust gas temperatures are usually much lower than 600°C, and therefore the ignition temperature of the particulate matter must be lowered in order to achieve combustion removal of the particulate matter in the exhaust gas flow.

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Incidentally, it has conventionally been known that catalysts carried on particulate matter filters can reduce the ignition temperature of the particulate matter, and for example, Japanese Examined Patent Publication HEI No. 7-106290 discloses a particulate matter filter carrying a mixture of a platinum-based

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metal and an alkaline earth metal oxide. With this particulate matter filter, the particulate matter ignites at a relatively low temperature of about 350-400°C, and is subsequently combusted in a continuous manner.

5 However, since the exhaust gas temperature during actual operation of a diesel engine is often below 350°C, it is impossible to achieve complete combustion removal of particulate matter at the aforementioned ignition temperature of about 350-400°C, and therefore pressure
10 loss of the exhaust gas through the filter increases, creating the problem of fuel efficiency reduction. Moreover, combustion of abundant residue of particulate matter leads to exposure of the particulate matter filter to temperatures of above approximately 800°C, resulting
15 in problems such as more rapid deterioration of the particulate matter filter.

IT is therefore an object of the present invention to provide a particulate matter purifying catalyst which can easily oxidize particulate matter collected on particulate matter filters at a much lower temperature than is possible by the prior art.

Disclosure of the Invention

25 The object of the present invention is achieved by a particulate matter purifying catalyst characterized by comprising an NO oxidation catalyst wherein the catalyst component is carried on an acidic first carrier, and an NO₂ decomposition catalyst wherein the catalyst component is carried on a second carrier.

30 That is, the invention relates to a catalyst comprising both an NO oxidation catalyst and an NO₂ decomposition catalyst, wherein the catalytic effects of both the NO oxidation and NO₂ decomposition are combined to promote oxidation of particulate matter.

35 The action mechanism of the catalyst of the invention is believed to be as follows.

The NO oxidation catalyst promotes the following

reaction.



The NO_2 decomposition catalyst promotes the following reaction, releasing active oxygen (O').



Active oxygen exhibits extremely high activity for oxidation of particulate matter.

The active oxygen is produced by the following O_2 dissociation reaction.



However, the reaction rate of chemical equation (3) is much lower than the reaction rate of chemical equation (2) at temperatures under about 300°C . Consequently, while the NO in diesel engine exhaust gas is at a lower concentration than O_2 , acceleration of the aforementioned reactions (1) and (2) effectively promotes combustion of the particulate matter.

15 The NO oxidation catalyst of the invention having a construction with a catalyst component such as platinum carried on an acidic carrier is capable of notably accelerating the reaction of (1) above. This is because the catalyst component resides on an acidic carrier, i.e., the catalyst component such as platinum is exposed to an acidic condition by the action of the acidic carrier, such that the acidic NO_2 produced by oxidation is easily released from the catalyst component.

20 Consequently, a large amount of NO_2 is supplied from the NO oxidation catalyst by reaction (1), after which the decomposition catalyst component produces active oxygen from the NO_2 by reaction (2), thereby allowing efficient supply of a large amount of active oxygen from the NO contained in the exhaust gas, so that the particulate matter can be oxidized at a high rate even when the exhaust gas temperature is below approximately 300°C .

25 The present inventors believe the particulate matter

oxidation mechanism to be as follows. The particulate matter structure is a structure comprising aggregates of fine planar hexagonal graphite, and since the number of carbon bonds is lower at the edge sections thereof, the 5 pi electron density of the bonds is higher than at the plane sections. For this reason, the electrophilic active oxygen O[•] is attracted to the high electron dense sections and attacks the carbon bonds, oxidizing them. That is, it is thought that the particulate matter with a 10 graphite structure is readily oxidized by the essentially electrophilic active oxygen, and therefore the abundant production of active oxygen promotes low-temperature particulate matter oxidation.

15 Brief Description of the Drawings

Fig. 1(a) is a schematic illustration of a wall cross-section of a monolith filter carrying the catalysts of the invention.

20 Fig. 1(b) is a schematic illustration of a cross-section of a monolith filter carrying the catalysts of the invention.

Fig. 2(a) is a schematic illustration of a coated layer interior carrying the catalysts of the invention.

25 Fig. 2(b) is a schematic illustration of a coated layer interior carrying the catalysts of the invention.

Best Mode for Carrying Out the Invention

The NO oxidation catalyst constituting one of the particulate matter purifying catalysts of the invention 30 comprises a catalyst component with NO oxidation performance such as platinum, gold, ruthenium, rhodium, iridium, palladium or the like, carried on an acidic carrier. As acidic carriers there may be mentioned 35 powders composed of particles with homogeneous components, such as silica, silica-alumina and zeolite with an SiO₂/Al₂O₃ ratio of 40 or greater.

The acidic carrier may also be tungstic

acid/zirconia, antimonic acid/alumina or the like, prepared by coating weakly acidic or amphoteric particles such as zirconia or alumina with an acidic substance such as tungstic acid or antimonic acid. These may be 5 obtained, for example, by immersing zirconia or alumina in an ammonium metatungstate aqueous solution as a tungstic acid precursor or an antimony sulfate aqueous solution as an antimonic acid precursor, evaporating to dryness, and then firing.

10 The catalyst component such as platinum may be loaded on the acidic carrier by evaporative drying, precipitation, adsorption, ion-exchange, reductive deposition or the like.

15 The NO_2 decomposition catalyst constituting the other particulate matter purifying catalyst of the invention has the catalyst component carried on a second carrier. This catalyst component may be selected as desired from the group of transition metals, among which there may be mentioned iron, manganese, cobalt, copper, 20 nickel, vanadium, yttrium, zinc, niobium and molybdenum.

25 The catalyst component of the NO_2 decomposition catalyst may also be at least one type of metal selected from among alkali metals and alkaline earth metals, among which there may be selected as desired, lithium, sodium, potassium, rubidium, cesium, francium, beryllium, magnesium, calcium, strontium, barium and the like.

30 It was found that when an alkali metal or alkaline earth metal is used as the catalyst component of the NO_2 decomposition catalyst, the NO_2 decomposition is further promoted if it is carried together with a precious metal selected from the group consisting of platinum, gold, ruthenium, rhodium, iridium, palladium and mixtures thereof.

35 No particular restrictions are required for the second carrier on which the catalyst component of the NO_2 decomposition catalyst is carried, but it is preferably selected from among weakly acidic or amphoteric

substances such as titania, zirconia, titania-zirconia, alumina, silica and the like.

5 Loading of the catalyst component of the NO₂ decomposition catalyst on the second carrier may be accomplished in the same manner as the NO oxidation catalyst, by evaporative drying, precipitation, adsorption, ion-exchange, reductive deposition or the like using, for example, a solution of the catalyst component.

10 The proportion of the components of the particulate matter purifying catalyst of the invention is not particularly restricted, but an NO oxidation catalyst/NO₂ decomposition catalyst ratio of 1/6-6/1 and especially 1/3-3/1, in terms of weight, is preferred. The catalyst component in the NO oxidation catalyst constitutes 15 preferably 0.5-10 parts by weight and more preferably 1.5-3 parts by weight to 100 parts by weight of the acidic carrier. The catalyst component in the NO₂ decomposition catalyst constitutes preferably 1-40 parts by weight and more preferably 2-10 parts by weight to 100 parts by weight of the second carrier.

20 The particulate matter purifying catalyst of the invention is carried on a particulate matter filter, to allow promotion of continuous oxidation of particulate matter collected on the particulate matter filter.

25 The particulate matter filter may be, for example, a cordierite monolith filter, and an embodiment of a filter using the catalyst of the invention is shown in Fig. 1.

30 In this embodiment, the NO oxidation catalyst and NO₂ decomposition catalyst of the invention reside as a coated layer covering the wall columns of the monolith filter. In the coated layer, the NO oxidation catalyst and NO₂ decomposition catalyst may reside in a randomly mixed state as shown in Fig. 2(a), or they may reside in 35 layers as shown in Fig. 2(b).

Examples

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-- Effect of carrier on NO oxidation performance --

5 Tungstic acid/zirconia (WO_3/ZrO_2), silica, silica-alumina, MFI zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$), dealuminized Y zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$), γ -alumina, zirconia and Ba/ γ -alumina were prepared as carriers, and after coating each of the carriers onto monolith substrates, each carrier was impregnated with a dinitrodiamine Pt solution and subjected to drying and prefiring followed by 1 hour of firing at 650°C to obtain catalysts with 2 g of Pt loaded 10 on each carrier per liter volume of monolith substrate.

15 The WO_3/ZrO_2 was the carrier for the NO oxidation catalyst, prepared by the method of Example 1 described below. The Ba/ γ -alumina was the carrier prepared by the method of Comparative Example 1.

15 The catalysts were each subjected to a stream of gas with the composition shown below, and the $\text{NO} \rightarrow \text{NO}_2$ oxidation rate was measured at gas temperatures of 200°C and 250°C. The results are shown in Table 1.

20 Gas composition: 250 ppm NO + 1 ppm SO_2 + 5% H_2O + 6% CO_2 + 6% O_2 (remainder: nitrogen)

Table 1 Comparison of NO oxidation performance

Catalyst carrier	NO oxidation rate (%)	
	200°C	250°C
WO_3/ZrO_2	64	93
Silica	45	92
Silica-alumina	34	92
MFI zeolite	66	92
Y zeolite	62	93
γ -alumina	15	90
Zirconia	17	90
Ba/ γ -alumina	8.5	20

Catalyst component: 2 g Pt/1L monolith

25 The results shown in Table 1 demonstrate that the acidic carriers WO_3/ZrO_2 , silica, silica-alumina, MFI zeolite and dealuminized Y zeolite exhibited notably higher NO oxidation rates at 200°C compared to the γ -

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alumina (amphoteric), zirconia (weakly acidic) and Ba/ γ -alumina (basic). The reason for the extremely low NO oxidation rate of Ba/ γ -alumina is believed to be inhibition of Pt oxidation performance by the basic Ba.

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Example 1

After adding 20 parts by weight of an ammonium metatungstate aqueous solution containing WO₃ at a 50 wt% concentration to 91 parts by weight of zirconium hydroxide powder, the resulting mixture was dried overnight at 80°C and then fired at 650°C for 2 hours to obtain tungstic acid/zirconia (WO₃/ZrO₂) powder.

10 Separately, 85 parts by weight of a 40 wt% barium acetate aqueous solution was added to 100 parts by weight of γ -alumina powder, and the resulting mixture was dried overnight at 80°C and then fired at 500°C for 1 hour to obtain Ba/ γ -alumina powder.

15 To 100 parts by weight of the WO₃/ZrO₂ powder and 100 parts by weight of the Ba/ γ -alumina powder there were added 60 parts by weight of a 40 wt% concentration aluminum nitrate solution, 40 parts by weight of ceria/zirconia powder and 200 parts by weight of water, and the components were mixed with a ball mill for 8 hours.

20 25 The resulting slurry was coated and dried onto a monolith substrate, and then fired at 650°C for 1 hour to form a layer containing WO₃/ZrO₂ powder and Ba/ γ -alumina powder on the monolith substrate.

30 Next, the layer was impregnated with a dinitrodiamine Pt aqueous solution, and then further impregnated with a Rh nitrate aqueous solution and fired at 500°C for 1 hour to obtain a catalyst according to the invention carrying 2 g of Pt and 0.1 g of Rh per liter of monolith substrate.

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Example 2

WO₃/ZrO₂ powder was obtained in the same manner as Example 1.

After separately impregnating 100 parts by weight of γ-alumina powder with a solution containing 5 wt% Fe, the powder was dried overnight at 80°C and then fired at 500°C for 1 hour to obtain Fe/γ-alumina powder.

To 100 parts by weight of the WO₃/ZrO₂ powder and 100 parts by weight of the Fe/γ-alumina powder there were added 60 parts by weight of aluminum nitrate solution, 40 parts by weight of ceria/zirconia powder and 200 parts by weight of water, in the same manner as Example 1, and the components were mixed with a ball mill for 8 hours.

The resulting slurry was coated and dried onto a monolith substrate, and then fired at 650°C for 1 hour to form a layer containing WO₃/ZrO₂ powder and Fe/γ-alumina powder on the monolith substrate.

Next, in the same manner as Example 1, the layer was impregnated with a dinitrodiamine Pt aqueous solution, and then further impregnated with a Rh nitrate aqueous solution and fired at 500°C for 1 hour to obtain a catalyst according to the invention carrying 2 g of Pt and 0.1 g of Rh per liter of monolith substrate.

Comparative Example 1

After adding 85 parts by weight of a 40 wt% barium acetate aqueous solution to 100 parts by weight of γ-alumina powder, the resulting mixture was dried overnight at 80°C and then fired at 500°C for 1 hour to obtain Ba/γ-alumina powder.

To 100 parts by weight of the Ba/γ-alumina powder there were added 30 parts by weight of a 40 wt% concentration aluminum nitrate solution, 20 parts by weight of ceria/zirconia powder and 100 parts by weight of water, and the components were mixed with a ball mill

for 8 hours.

The resulting slurry was coated and dried onto a monolith substrate, and then fired at 650°C for 1 hour to form a layer containing Ba/ γ -alumina powder.

5 Next, the layer was impregnated with a
dinitrodiamine Pt aqueous solution, and then further
impregnated with a Rh nitrate aqueous solution and fired
at 500°C for 1 hour to obtain a comparison catalyst
carrying 2 g of Pt and 0.1 g of Rh per liter of monolith
substrate.

Comparative Example 2

To 100 parts by weight of silica powder there were added 30 parts by weight of a 40 wt% concentration aluminum nitrate solution, 20 parts by weight of ceria/zirconia powder and 100 parts by weight of water, and the components were mixed with a ball mill for 8 hours.

The resulting slurry was coated and dried onto a monolith substrate, and then fired at 650°C for 1 hour to form a layer containing silica powder.

Next, the layer was impregnated with a dinitrodiamine Pt aqueous solution, and then further impregnated with a Rh nitrate aqueous solution and fired at 500°C for 1 hour to obtain a comparison catalyst carrying 2 g of Pt and 0.1 g of Rh per liter of monolith substrate.

The catalyst with Pt and Rh carried on the acidic silica carrier was used for a comparative test in a system with NO_x production by NO oxidation carried out upstream, and particulate matter combustion carried out downstream.

-- Comparison of NO_x decomposition performance --

The proportion of NO_x decomposed to NO by the catalysts of Examples 1-2 and Comparative Examples 1-2 above was measured using diesel engine exhaust gas. Lean (air/fuel ratio = 30) and rich (air/fuel ratio = 14)

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operating conditions were employed, repeatedly alternated for 30 seconds and 1 second, respectively, and the NO₂ decomposition rate was measured based on the exhaust gas composition shown below, under lean conditions. The
 5 results are shown in Table 2. For the catalyst of Comparative Example 2, there was provided a particulate matter-accumulated monolith filter (without catalyst) downstream from the catalyst, and the NO₂ decomposition rate as measured at the outlet port of the monolith
 10 filter.

Gas composition: 250 ppm NO + 1 ppm SO₂ + 5% H₂O + 6% CO₂ + 6% O₂ (remainder: nitrogen)

Table 2 Comparison of NO₂ decomposition performance

	Catalyst		NO ₂ decomposition rate (%)	
	NO oxidation catalyst	NO ₂ decomposition catalyst	200°C	250°C
Example 1	Pt/WO ₃ /ZrO ₂	Pt/Ba/ γ -alumina	85	94
Example 2	Pt/WO ₃ /ZrO ₂	Fe/ γ -alumina	88	90
Comp. Ex. 1	Pt/Ba/ γ -alumina		78	88
Comp. Ex. 2	Upstream Pt/silica + monolith filter		2.1	3.5

15 Catalyst components: (2 g Pt + 0.1 g Rh)/1L monolith

The results shown in Table 2 demonstrate that the catalysts of the invention exhibit very high NO₂ decomposition performance even at temperatures below 200°C. On the other hand, with Comparative Example 1 which had Pt and Ba both present on the γ -alumina carrier, the NO₂ decomposition performance was slightly lower than that of the catalysts of the invention. The catalyst of Comparative Example 2 exhibited absolutely no NO₂ decomposition performance. The reason is believed to be its structure wherein no catalyst was carried on the monolith filter.

-- Comparison of particulate matter oxidation rates --

30 The particulate matter oxidation rates of the catalysts of Examples 1-2 and Comparative Examples 1-2 above were measured using diesel engine exhaust gas. The

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operating conditions were continuous lean conditions (air/fuel ratio = 30), where the particulate matter-containing exhaust gas with the composition shown below was fed to the catalyst-carrying particulate matter filter, and the particulate matter combustion rate was calculated from the particulate matter supply rate under conditions with the filter pressure loss at equilibrium. The results are shown in Table 3.

Gas composition: 250 ppm NO + 1 ppm SO₂ + 5% H₂O + 10 6% CO₂ + 6% O₂ (remainder: nitrogen)

Table 3 Comparison of particulate matter (PM) combustion rates

	Catalyst		PM combustion rate (mg/sec/L)	
	NO oxidation catalyst	NO ₂ decomposition catalyst	200°C	250°C
Example 1	Pt/WO ₃ /ZrO ₂	Pt/Ba/ γ -alumina	0.04	0.12
Example 2	Pt/WO ₃ /ZrO ₂	Fe/ γ -alumina	0.04	0.11
Comp. Ex.1	Pt/Ba/ γ -alumina		0.012	0.05
Comp. Ex.2	Upstream Pt/silica + monolith filter		0.002	0.006

Catalyst components: (2 g Pt + 0.1 g Rh)/1L monolith

The results shown in Table 3 demonstrate that the catalysts of the invention exhibited a notably higher particulate matter oxidation rate than the catalyst of Comparative Example 1, clearly showing the effect on particulate matter oxidation by the catalysts of the invention comprising both an NO oxidation catalyst and an NO₂ decomposition catalyst. Although the catalyst of Comparative Example 1 exhibited high NO₂ decomposition performance, as shown in Table 2, the particulate matter oxidation rate was lower than that of the catalysts of the invention. This is believed to indicate that the NO oxidation performance shown in Table 1 is one factor controlling active oxygen production at low temperature, and is important for oxidation of particulate matter.

Comparative Example 2 exhibited a very low oxidation rate, and the reason is believed to be that no active oxygen was released because of the absence of an NO₂

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decomposition catalyst, and therefore oxidation was promoted only by the reactivity between the NO₂ and particulate matter. It is thought that according to the invention, however, wherein NO oxidation and NO₂ decomposition were repeatedly accelerated in the catalyst, the resulting abundant active oxygen produced at low temperature considerably enhanced the particulate matter oxidation rate.

10 Industrial Applicability

As explained above, the present invention provides an effect whereby particulate matter emitted from diesel engines can be combusted at much lower temperatures than according to the prior art.